Small atom diffusion and breakdown of the Stokes–Einstein relation in the supercooled liquid state of the $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$ alloy

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Be diffusivity data in the bulk metallic glass forming alloy $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$ are reported for temperatures between 530 and 710 K, extending 85 K into the supercooled liquid state of the alloy. At the glass transition temperature T_g, a change in temperature dependence of the data is observed, and above T_g the diffusivity increases more quickly with temperature than below. The data in the supercooled liquid can be described by a modified Arrhenius expression based on a diffusion mechanism suggested earlier. The comparison with viscosity data in the supercooled liquid state of $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$ reveals a breakdown of the Stokes–Einstein relation, indicating a cooperative diffusion mechanism in the supercooled liquid state of $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$.
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Multicomponent deep eutectic metallic systems based on early transition metals often exhibit superior glass forming abilities[1–5] and an excellent stability with respect to crystallization in the supercooled liquid state above the glass transition. The latter enables many properties to be measured in this state of metallic systems which were experimentally inaccessible before.

In a recent publication[6] the authors demonstrated that it is possible to measure atomic diffusion in the supercooled liquid state (SLS) of the bulk glass forming metallic $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy,[3] using Be as the diffusing species. We suggested that diffusion of these small atoms in the SLS is based on a superposition of single atomic jumps of Be and a cooperative motion of neighbor atoms of Be that supports diffusion by increasing the frequency of critical free volume fluctuations. This leads to a modified Arrhenius expression to describe the temperature-dependent diffusivity of Be in the SLS, D_{SLS}, and probably other atoms which are small enough to perform single atomic jumps in the SLS,[6,7]

$$D^{\mathrm{SLS}}(T)=D_0^{\mathrm{SS}}\exp\left(-\frac{\Delta H_M^{\mathrm{SS}}}{k_BT}\right)\exp\left(\frac{N}{N_A}\frac{\Delta S^{\mathrm{SLS}}(T)}{k_B}\right). \quad (1)$$

Here D_0^{SS} and ΔH_M^{SS} are the pre-exponential and migration enthalpy in the solid state (SS) below the glass transition, $\Delta S^{\mathrm{SLS}}(T)$ is the configurational (''communal'') entropy of the supercooled liquid, N is the typical number of nearest- and next-nearest-neighbor atoms which influence the jump of a Be atom by their viscous rearrangements, and N_A is Avogadro's number. This picture does not require a detailed modeling of the SLS because it takes advantage of a measurable quantity, the communal entropy, to describe the SLS.

Since the data in Ref. 6 are still limited to a relatively small temperature interval above T_g, measurements on metallic alloys with even higher stability in the SLS are desirable. Investigations of small atom diffusion in metallic alloys with different kinetics in the SLS (leading to different degrees of temperature dependence of ΔS^{SLS}) can confirm the connection of diffusivity and communal entropy, as suggested by Eq. (1). Systematic studies of the diffusion of atomic species with different masses, e.g., through the isotope effect,[8] can reveal the mutual importance of single jump and cooperative effects in the SS and SLS. In particular, for larger atoms no significant single jump contribution to diffusion should be expected.[9]

The approach reported in this letter combines the first two points. We chose another member of the ZrTiNiCuBe bulk glass family, $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$, for investigations of Be diffusion in the SS and SLS. Differential scanning calorimetry analysis of this particular alloy shows a higher thermal stability of the SLS with respect to crystallization.[10] Like $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$, $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$ exhibits chemical decomposition upon annealing[10,11] which limits the annealing times and temperatures;[7] but, the time and temperature windows within which Be diffusion measurements in this alloy are possible without a visible influence of decomposition are substantially wider than in $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$. The change of specific heat capacity at T_g of $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$ is $\Delta c_p(T_g)=1k_B$/atom, which is a factor of 2.9 smaller than that of $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$. The difference in the slope at T_g of the entropy versus temperature functions of the SLS and SS, $\Delta c_p(T_g)/T_g$, is therefore by the same factor

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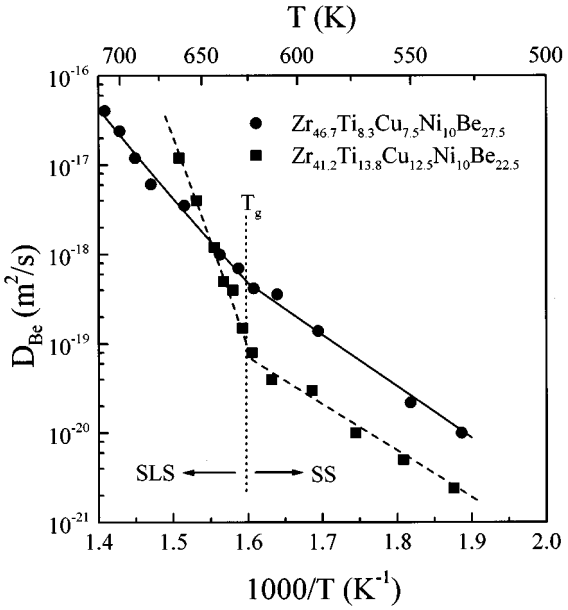

FIG. 1. Be diffusivity data in $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$ (solid circles) and $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ (solid squares, Ref. 6). The isothermal glass transition temperature T_g is about 625 K in both cases. The solid line shows the fitting result according to Eq. (2) for $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$ ($D_0^{SS}=8\times10^{-10}$ m^2/s, $\Delta H_M^{SS}=1.1$ eV/atom, and $N=13$).

smaller than in $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$, provided that the isothermal glass transition temperatures are identical. All experimental procedures for determination of Be diffusivity by high-energy elastic backscattering and Δc_p measurements have been discussed before.[6,12,13] Finally, we compare our diffusion data with recently published viscosity data[14] in order to examine the validity of the Stokes–Einstein relation[15] for atomic transport in the SLS of $Zr_{42.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$.

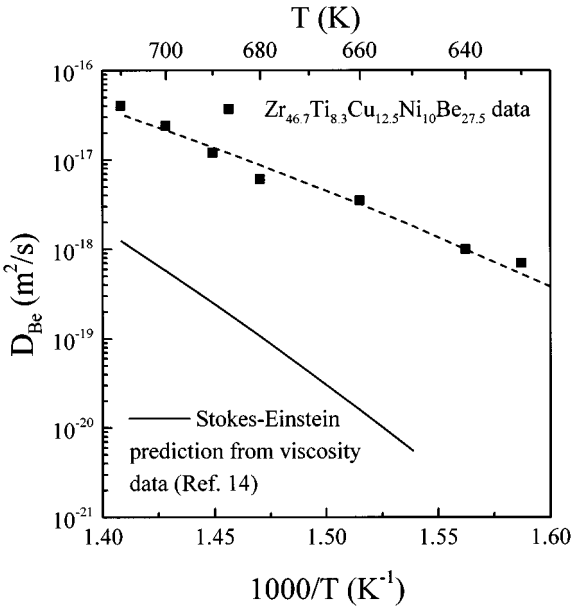

FIG. 2. Beryllium diffusivity data in the supercooled liquid state of $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$ and Stokes–Einstein prediction [Eq. (3), $R=1.1$ Å] for diffusivity, as calculated from the Vogel–Fulcher fit for viscosity data (Ref. 14) of $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$ (solid line).

Figure 1 shows an Arrhenius plot of the Be diffusivity in $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$, in comparison with the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ data.[6] No dependence of the diffusivity data on the duration of heat treatment, indicating structural relaxation[9] or decomposition effects[10,11] in $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$, was observed within the time scale of the annealing treatments. $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$ shows an increase in the temperature dependence of D_{Be} at about the same temperature that $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ does. We associate this temperature (~625 K) with the isothermal T_g of $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$. Below T_g the data follow an Arrhenius law with a migration enthalpy which is about the same as in $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$. The Be diffusivity is some 10 times higher than for $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$, and the increase in temperature dependence of D_{Be} at T_g is distinctly smaller in $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$ than in $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$. Fitting an Arrhenius law to the data above T_g results in values $Q=1.9$ eV/atom and $D_0=1.7\times10^{-3}$ m^2/s. Fitting Eq. (1) to all data with

$$\Delta S^{SLS}(T)\approx\frac{\Delta c_p(T_g)}{T_g}(T-T_g)$$

$$=\frac{1k_B\ \text{atom}^{-1}N_A}{T_g}(T-T_g)\quad\text{for } T\geqslant T_g, \qquad (2)$$

$$\Delta S^{SLS}(T)=0\quad\text{for } T<T_g,$$

covers both the Arrhenius fit below T_g and the modified Arrhenius fit according to Eq. (1) above T_g. It leads to $D_0^{SS}=8\times10^{-10}$ m^2/s, $\Delta H_M^{SS}=1.1$ eV/atom, and $N=13$. The fitting curve is also shown in Fig. 1 (solid line).

As in $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$, the small values for D_0^{SS} and ΔH_M^{SS} indicate single atomic jumps of the small Be atoms in the SS of $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$. The difference of about one order in magnitude in the Be diffusivity for $T<T_g$ in both alloys is probably due to a higher fraction of free volume[16] in $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$. The average atomic volume of $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$, $\langle\Omega_2\rangle$, is higher than in $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ ($\langle\Omega_1\rangle$), $[\langle\Omega_2\rangle-\langle\Omega_1\rangle]/\langle\Omega_1\rangle=4\times10^{-3}$, and it seems plausible to assume that the average free volume is also higher in $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$. Diffusion depends exponentially on the amount of free volume.[17] This high sensitivity is responsible for the substantial decrease in diffusivity that can be observed during structural relaxation and annealing of excess free volume in rapidly quenched conventional metallic glasses.[9] Nevertheless, the higher free volume content of $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$ does not significantly influence the migration enthalpy, which is about the same as in $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$.

The data can be successfully fitted by Eq. (2) over the whole temperature regime investigated. This supports the suggested relationship between diffusion in the SLS and communal entropy.[6] According to this relationship, the smaller change in temperature dependence of the diffusivity at T_g in $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$ is caused by the less rapid increase of the communal entropy in the SLS of $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$ near T_g as indicated by the smaller $\Delta c_p(T_g)$. This means that the kinetics above but near T_g are

more sluggish in $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$ than in $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$. The fitting result for the number of neighbor atoms involved in Be diffusion in $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$, N, is smaller than in $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$. The order of magnitude for N is reasonable, and its value $N=13$ again suggests a higher fraction of average free volume in $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$. In the less dense packed $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$ the critical free volume fluctuation required for the motion of Be can be achieved by the cooperative rearrangement of fewer atoms than in $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$.

Although Be diffusion in the SLS of $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$ could be measured over a temperature interval 2 times wider than in $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$, no concave curvature of the $D_{\mathrm{Be}}(T)$ relation (see Fig. 4 of Ref. 6), as expected from the concave curvature of $\Delta S^{\mathrm{SLS}}(T)$, is indicated. This is probably also due to the sluggish kinetics near T_g in the SLS of $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$ which makes the $\Delta S^{\mathrm{SLS}}(T)$ curve bend at higher temperatures than in $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$.

The present diffusivity data and the equilibrium viscosity data of $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$ in the SLS (Ref. 14) overlap in the temperature regime 650–710 K. Thus, we can check the Stokes–Einstein relation[15] for atomic transport in the SLS of $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$ at these temperatures.

Figure 2 shows our measured data and the diffusivity as predicted by the Stokes–Einstein relation for translational diffusion,

$$D(T)=\frac{k_B T}{6\pi[\eta(T)]R}, \tag{3}$$

by choosing the atomic radius of Be, 1.1 Å, for the molecular radius R and using the calculated $\eta(T)$ from the Vogel–Fulcher fit to the experimentally determined viscosity.[14] According to Fig. 2, the Be diffusion is much faster in comparison to the prediction of Eq. (3). The order of magnitude predicted by Eq. (3) is only similar to the data when subangstrom R values are used, but then Eq. (3) still predicts a faster decrease of diffusivity with temperature than measured. With increasing temperature the difference between the measured data and the Stokes–Einstein prediction tends to decrease.

The Stokes–Einstein relation is based on the assumption that the diffusing atom behaves as a Brownian particle which moves slowly and with constant velocity in a viscous medium, experiencing a frictional force given by Stokes's law. It thus rests on the idea that the diffusing object is much larger than the constituents of the medium. Although this view cannot strictly be correct for atomic and molecular diffusion, the relation has been successful in correlating measurements of $D(T)$ and $\eta(T)$ for many liquids.

In some organic glasses a breakdown of the Stokes–Einstein relation at temperatures near but above T_g has been reported and attributed to cooperative behavior in the supercooled liquid.[18] In these cases the measured data are also higher than those predicted by the Stokes–Einstein relation, and the decrease of translational diffusivity with temperature is also slower than predicted by the Stokes–Einstein relation. In all cases, including the supercooled liquid $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$ alloy, the viscous medium does not only hinder the diffusing atom's movement by producing a frictional force, but apparently increases diffusion by 1–2 orders of magnitude when compared to the Stokes–Einstein prediction for the investigated temperature regime. We believe that the observed breakdown of the Stokes–Einstein relation is another indication for the proposed cooperative diffusion mechanism[6] in the SLS of ZrTiCuNiBe bulk glass formers.

In summary, the Be diffusivity in the solid and the supercooled liquid states of the bulk glass forming metallic $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$ alloy shows a similar change in temperature dependence at the glass transition temperature as that in the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy. The data can be described by a modified Arrhenius expression suggested earlier. A comparison with viscosity data reveals a breakdown of the Stokes–Einstein relation in the supercooled liquid state of $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$, and the measured diffusivity values are much higher than predicted by the Stokes–Einstein relation. These results support the recently suggested diffusion mechanism for small atoms in the supercooled liquid state of and the relation between diffusivity and configurational entropy.

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